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(54) Fabric-cleaning compositions

(57) The invention is concerned with post-foaming cleaning compositions which may be dispensed from a pressurised container. The compositions contain a post-foaming agent, for example a volatile hydrocarbon which boils and causes the composition to fizz on the

surface of a fabric to be cleaned thereby enhancing the cleaning effect. The compositions contain high amount of volatile hydrocarbon, i.e. about 20 to 40% by weight.

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[0002] Post-foaming cleaning compositions are known in the art. Such compositions contain a post-foaming agent, typically a hydrocarbon that is volatile at room temperature and pressure, that boils when discharged from a container causing the composition to foam. Typical post-foaming cleaning compositions are disclosed in US patents 6,004,920, 5,962,396 and 6,051,542.

[0003] The post-foaming compositions described in the aforementioned patents contain relatively low amounts of volatile hydrocarbon, i.e. about 7 to 14% by weight of iso-pentane. This relatively low amount of post-foaming agent limits the cleaning effect of such compositions. In addition, the low quantities of volatile hydrocarbon are insufficient to provide the composition with satisfactory propellant effect in order to discharge itself effectively from its container upon actuation of the container. Accordingly, not only do such compositions have limited cleaning effect, they must be packaged in containers which provide propellant means external of the composition. Such containers, e.g. the so-called bag-in-can containers are relatively expensive compared with standard aerosol canisters.

[0004] However, as one attempts to incorporate higher amounts of volatile hydrocarbon into post-foaming cleaning compositions, so the volatile hydrocarbon displays an increased tendency to form a separate phase from the remaining components of the composition. This is undesirable because phase-separated hydrocarbon does not have as effective a cleaning or foaming effect as hydrocarbon mixed or dissolved in the composition. Accordingly, whereas phase-separated hydrocarbon could act as a propellant, its cleaning or foaming effect would not be in proportion to the increase in the amounts of hydrocarbon employed.

[0005] Accordingly, there remains a need to provide cleaning compositions with efficient cleaning power that may be dispensed from relatively cheap pressurised containers.

[0006] It has now been found that it is possible to produce a composition containing post-foaming and propellant quantities of liquid hydrocarbon that is stable to phase separation.

[0007] The invention therefore provides in a first aspect a post-foaming cleaning composition comprising a post-foaming agent in an amount of at least 20% and more preferably from 20 to 40% by weight based on the total weight of the composition.

[0008] The post-foaming agent may be dissolved or mixed in the composition in higher amounts than have heretofore been possible. When discharged onto a surface to be cleaned the composition penetrates the surface whereupon the post-foaming agent boils causing the composition to foam vigorously and for extended periods of time, e.g. for up to 15 minutes. Vigorous foaming not only provides a visible and audible key which suggests to the user that the composition is working effectively, it also, by virtue of the mechanical action of the foam on the surface to be cleaned, facilitates and enhances the cleaning action. In contrast, if the post-foaming agent is substantially phase-separated in the dispensing device, it will be dispensed separately from the remainder of the composition. In addition to the reduced cleaning or foaming effect aforementioned, the dispensed free post-foaming agent is unsightly for the user and suggests that the composition has malfunctioned.

[0009] In a preferred embodiment of the invention the post-foaming agent is a hydrocarbon, and may be any of those hydrocarbons that are volatile at room temperature and pressure and which are useful as post-foaming agents and propellants, for example a saturated aliphatic hydrocarbon having from 4 to 5 carbon atoms, more particularly n-butane, iso-butane, n-pentane or iso-pentane, or mixtures thereof. Most preferred is n-pentane.

[0010] A composition according to the invention may have the form a low viscosity free-flowing liquid. The viscosity should be such that when dispensed, the composition is mobile, in order that it may wet and penetrate readily into the surface to be cleaned, e.g. the surface of a fabric, such that the foaming occurs substantially within the weave of the fabric thereby to mechanically agitate the fabric for better stain removal. The foam produced by the composition should be rather mobile and unstable. Rigid, stable foams, typical of the gel-like foamable compositions in the prior art, would have the disadvantage of holding or lifting large amounts of the cleaning actives away from the surface to be cleaned. Stable foams would also contribute to undesirable foaming in a washing machine used to clean a fabric subsequent to its treatment with a post-foaming composition.

[0011] Preferred compositions according to the invention have a viscosity at 25°C of up to about 400 centipoise, more particularly 250 to 350 centipoise.

[0012] Compositions according to the invention may contain any of those components employed in post-foaming cleaning compositions known in the art. Typically a composition may comprise a hydrophobic component, a hydrophilic component, a surfactant component, and other adjuvants or additives commonly employed in the art.

[0013] The hydrophilic component is water, e.g. de-ionised water, preferably present in amounts of about 20 to 40% by weight of the total composition.

[0014] As hydrophobic component there may be mentioned those water insoluble saturated or unsaturated organic compounds having from 4 to 30 carbon atoms commonly used in the formation of an oil-phase. Preferred as the hy-

[0015] The surfactant component comprises a fatty alcohol alkoxylate, more particularly a C13 to C15 fatty alcohol ethoxylate. The ethylene oxide (EO) content of the fatty alcohol ethoxylate may vary between 1 to 5 EO units per fatty alcohol unit, more particularly, 3 EO units per fatty alcohol unit. The fatty alcohol ethoxylate preferably has an Hydrophilic Lipophilic Balance (HLB) of about 4 to 10. A suitable example is Lutensol AO3®, BASF AG, Ludwigshafen, Germany.

[0016] The presence of the fatty alcohol alkoxylate is believed to play an important role in stain removal and stabilising the composition, that is, it offers classical detergency properties and also assists in the formation of a composition comprising high amounts of post-foaming agent, and reduces the tendency for the post-foaming agent to form a sep-

arate phase. The precise amounts of fatty alcohol alkoxylate needed to provide a stain-removing and stabilising effect may vary within wide limits depending on the nature and amount of other components present in the composition. However, having been apprised of the significance this component, the skilled person would be able to experiment without undue burden to determine an appropriate quantity of this component for a given composition.

[0017] Preferred compositions according to the invention contain fatty alcohol alkoxylate, e.g. fatty alcohol ethoxylate in an amount of greater than about 7% by weight, more particularly about 7 to 13% by weight of the total composition. Within this preferred range, higher amounts of surfactant promote stability of the composition. However, if the amount of surfactant exceeds the upper limit the stain-removing effect when a treated fabric is washed diminishes.

[0018] The surfactant component may comprise a mixture of surfactants, thus in a preferred embodiment the composition comprises a first and second surfactant component.

[0019] The first surfactant component is a fatty alcohol ethoxylate as hereinabove described.

[0020] The second surfactant component may be a fatty alcohol alkoxylate and is different from said first surfactant component. It may be any of those primary aliphatic alcohol alkoxylates known for use in stain removing compositions in the art. Preferably the second surfactant component is a C12-C18 semi-linear fatty alcohol ethoxylate butoxylate, which preferably has a cloud point in water of between 28 and 42°C. A particularly preferred second surfactant component is Plurafac LF221 from BASF AG.

[0021] The second surfactant component may be employed in amounts of about 1.5 to 2.5% by weight, more particularly about 1.9 to 2.3 % by weight based on the total weight of the composition.

[0022] The composition may comprise other adjuvants that serve to stabilise the interfacial tension between the hydrophilic and hydrophobic components. These components are often referred to as co-surfactants and co-solvents. The composition may comprise one or more of these co-surfactants in appropriate quantities to achieve a stabilised composition. The nature and precise quantities of co-surfactants used in a composition may be determined by the skilled person without undue burden and using only routine experimentation, having regard to the nature and relative proportions of the hydrophilic and hydrophobic components.

[0023] The compositions preferably employ first and second co-surfactants. Said first co-surfactant may be selected from any of those di-alkylsulphosuccinates known in the art. More particularly, the first co-surfactant is a sodium dialkyl sulphosuccinate, e.g. sodium dioctylsulphosuccinate. The first co-surfactant may be employed in amounts of about 1.9 to 2.4% by active weight based on the total weight of the composition. Preferably the first co-surfactant is Rewopol SBDO 75, Goldschmidt AG, Germany.

[0024] A second co-surfactant may be selected from any of the long chain unsaturated fatty acids useful as co-surfactants, in particular C₁₆ to C₁₈ unsaturated fatty acids, more particularly oleic acid. Said second co-surfactant may be employed in amounts of about 2.5 to 3.1% by active weight based on the total weight of the composition. Preferably said second co-surfactant is Priolene 6992, Uniquema, England.

[0025] A co-solvent may be selected from short-chained linear or branched aliphatic alcohols, e.g. iso-propanol. Said co-solvent may be present in amounts of about 7.5 to about 9.3% by weight of the total weight of the composition.

[0026] The pH of the composition is preferably in the range of about 8 to 9, more preferably 8.2 to 8.7. To maintain the composition at slightly alkaline pH it is preferred to employ an alkaline substance such as an alkali metal hydroxide, e.g. sodium hydroxide.

[0027] Additionally, compositions may comprise other additives or adjuvants commonly used in post-foaming cleaning compositions, for example preservatives or fragrances, provided that such agents do not adversely affect the properties of the composition. These additives may be employed in conventional amounts and preferably do not constitute more than about 1% by weight of the total composition, for example fragrances or preservatives may be added in small amounts, e.g. about 0.1 to 1.0% by weight and about 0.005 to about 0.1% by weight respectively.

[0028] In a preferred embodiment of the present invention there is provided a post-foaming cleaning composition comprising about 20 to 40 weight percent (wt%) of deionised water; 20 to 40 wt% n-butane; 15.75% to 19.25 wt% isoparaffinic hydrocarbon with a boiling point of 113 to 143°C; 7.5 to 9.3 wt% isopropanol; 7.1 to 13.0 wt% fatty alcohol ethoxylate (HLB 4 to 10); 2.5 to 3.1 wt % sodium di-alkyl sulphosuccinate (75%); 1.9 to 2.3 wt % of a fatty alcohol

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[0029] The hydrophilic component and the post-foaming agent are the components present in the greatest quantity in a composition of the present invention, and together they may consist of up to about 80% by weight of the composition. The ratio of these combined components (hereinafter A) to the remaining components with the exception of any fragrance and preservatives (hereinafter B) may vary within a wide range without affecting the stability or effectiveness of the composition. Preferably the weight ratio A:B may be from about 1.4:1 to about 1.1:1. Particularly preferred compositions comprise components A in an amount of about 58.126 weight percent and components B in an amount of about 41.650 weight percent; or, components A in an amount of about 55.126 weight percent and components B in an amount of about 44.650 weight percent; or components A in an amount of about 52.126 weight percent and components B in an amount of about 47.650 weight percent; or components A in an amount of about 52.126 weight percent and components B in an amount of about 47.650 weight percent. Any remaining mass is made up by fragrances and preservatives.

[0030] Compositions according to the invention are preferably microemulsions. Microemulsion compositions are preferably employed because of their ability to wet both hydrophobic and hydrophilic surfaces. This may be particularly beneficial when a fatty stain is to be cleaned from a hydrophilic surface presented by certain fabrics, e.g. cotton fabrics. [0031] A composition according to the invention may be made by any procedure commonly known in the art for the preparation of post-foaming cleaning compositions. A particular method comprises admixing all of the components with the exception of the post-foaming agent until a homogeneous mixture is formed. Thereafter, the mixture may be poured into a conventional aerosol can, a valve assembly fitted to the filled aerosol can and the post-foaming agent added in gaseous form using conventional high-pressure filling equipment. The packaged composition is thereby pressurised at a pressure such that the post-foaming agent is substantially all in the liquid phase and substantially all is dispersed or dissolved in the composition. In the case of n-butane, the post-foaming agent is added under a pressure of about 48 psi (3.3 X 10⁵ N/m²).

[0032] The invention provides in another of its aspects a packaged composition as hereinabove described. By a packaged is meant that the composition is provided in containers that are suitable for dispensing such cleaning compositions. Appropriate containers include those containers known in the art that are capable of withstanding cleaning compositions under pressure and include standard tin-plate aerosol cans that may or may not need to be internally lacquered or to be protected from corrosion by the inclusion of inhibitors in the composition.

[0033] Whereas the invention is primarily concerned with packaged compositions employing the relatively inexpensive standard aerosol containers, the compositions may also be packaged in the variety of containers known as bagin-can containers more fully described in US patent 4,964,540. The latter packaged compositions may not be as cost-effective as those employing aerosol canisters, but the dispensed compositions nevertheless realise substantially the same cleaning effect.

[0034] Packaged compositions according to the invention are monophasic, that is substantially all of the post-foaming agent is dissolved in, or mixed with, the compositions' other ingredients. A monophasic composition has the advantage that substantially all of the post-foaming agent will be discharged in admixture with the remainder of the composition. Accordingly, as the post-foaming agent boils it causes the composition to fizz and bubble more vigorously and for a longer period of time than would occur if significant amounts of the post-foaming agent were discharged separately.

[0035] Due to the relatively high amounts of hydrocarbon post-foaming agent dissolved in compositions according to the invention, the hydrocarbon may act as both post-foaming agent and propellant. This enables compositions according to the invention to be packaged in the relatively inexpensive standard aerosol containers as aforementioned. In such an embodiment, the hydrocarbon may be used as the sole propellant. Alternatively, additional propellants may be used, for example a container may be pressurised with propellant gases such as nitrogen, carbon dioxide, compressed air, halogenated compounds or nitrous oxide. Preferably any additional propellant would not be a volatile organic compound for environmental reasons.

[0036] Compositions according to the invention may be applied to surfaces that need to be cleaned to provide efficient pre-spotting, that is, the composition acts on a stain to start the cleaning process and to enable enhanced stain removal during a subsequent wash cycle. Compositions are particularly effective pre-spotters for oily stains, such as vegetable and motor oils, shoe polish and lipstick. The compositions may be used on a variety of fabrics such as cotton, polyester, wool, polyester/cotton, and polyester/wool. Microemulsion compositions are particularly useful as pre-spotters for oily stains on hydrophilic fabrics such as cotton due to the ability of microemulsions to wet both hydrophobic and hydrophilic surfaces.

[0037] There now follows a series of examples that serve to illustrate the invention.

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Example 1

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Formation of a post-foaming microemulsion composition

- [0038] The composition set forth hereinbelow was made according to the following procedure:
 - 1. Add deionised water into a main mixing vessel
 - 2. Add Bronopol with stirring
 - 3. Add the following materials in the order listed and ensure good agitation at 25°C until a homogenous solution is formed: NaOH; Isopropanol; Oleic Acid; C₁₃-C₁₅ linear alcohol ethoxylate 3EO (warm to 25°C before addition); C₁₃-C₁₅ linear alcohol ethoxylate butoxylate; Sodium di-octyl sulphosuccinate 75%; Fragrance.
 - 4. Finally add Isopar E with continuous stirring until the mixture is homogenous and clear at 22°C. Continue stirring for at least 15 minutes.
 - 5. Check pH of the mixture. Adjust to approx. 8.5 if necessary using 30% sodium hydroxide solution or oleic acid. Continue stirring for 20-30 minutes.

[0039] The mixture was poured into a glass aerosol bottle. A valve assembly was fitted over the aerosol bottle prior to introducing the n-butane under a pressure of 48psi. The n-butane dissolved fully in the composition and the final composition had the appearance of a monophasic solution.

	wt%
Deionised water	28.126
n-Butane	30.000
Isoparaffinic hydrocarbon Bpt.113-143	17.500
(ISOPAR E - Exxon Chemicals	
Isopropanol	8.400
C13-C15 linear alcohol ethoxylate 3EO	7.700
(Lutensol AO3. BASF)	
Sodium di-alkyl sulphosuccinate 75%	2.800
(Rewopol SBDO 75 Goldschmidt)	
Oleic acid	2.800
(Priolene 6992 - Uniqema)	
C13-C15 linear alcohol ethoxylate butoxylate	2.100
(Plurafac LF221, BASF)	
Sodium hydroxide 47%	0.350
Fragrance	0.210
Preservative	0.014
(Bronopol, BASF)	
pH of formula 8.2 -8.7	

Example 2

The effect of fatty acid ethoxylate concentration on appearance of compositions

[0040] The following compositions were formed according to the methodology of Example 1. The composition « D » corresponds to the composition of Example 1. All quantities are expressed in weight percent. The linear alcohol ethoxylate was Lutensol AO3 from BASF.

	Α	В	С	D	E
Deionised water	24.626	26.726	27.426	28.126	28.826
Butane 48psig	30.000	30.000	30.000	30.000	30.000
Isoparaffinic	17.500	17.500	17.500	17.500	17.500
hydrocarbon					,

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- '	A	В	C	D	E
Bpt.113-143					
Isopropanol	8.400	8.400	8.400	8.400	8.400
C13-C15 linear		1			
alcohol ethoxylate 3EO	11.200	9.100	8.400	7.700	7.000
Sodium di-alkyl	2.800	2.800	2.800	2.800	2.800
sulphosuccinate 75%		1			
Oleic acid	2.800	2.800	2.800	2.800	2.800
Fatty alcohol	2.100	2.100	2.100	2.100	2.100
alkoxylate				}	
Sodium hydroxide	0.350	0.350	0.350	0.350	0.350
47%					
Fragrance	0.210	0.210	0.210	0.210	0.210
Preservative	0.014	0.014	0.014	0.014	0.014

[0041] Compositions A, B, C and D when filled in glass aerosol bottles all gave single-phase systems. Formulation E demonstrated a significant layer of free hydrocarbon above the composition. This suggests that the linear alcohol ethoxylate should be present in an amount of greater than 7% by weight to obtain a monophasic composition.

[0042] Upon discharge from the aerosol container, compositions A, B, C and D all presented as a creamy liquid that bubbled for several seconds on contact with the fabric thus providing a good visible cue as to the cleaning effect. Composition E, however, lacked uniformity, presenting a clear liquid that was essentially pure hydrocarbon.

Example 3

Stain Pre-spotting performance

[0043] All fabric used for this test (100% white cotton) was washed to remove any 'finishing' treatment on the new material. This was done by washing 3-4m of fabric at 40°C (European washing machine) using 50g of non-biological washing powder (Persil automatic). The fabric was partially dried and then ironed to remove creasing. The fabric was then cut into swatches of 14.5cm by 22cm using a zig-zag scissors to prevent fraying. All swatches were ironed again and laid on a worktop ready for staining (matt side up to prevent excess 'wicking').

[0044] Since the compositions would be specifically targeted for removal of stubborn oily stains, the test focused on the four key oily stains which are difficult to remove in a standard wash, viz.

[0045] Vegetable oil - dyed using oil soluble brown dye - 1 drop 0.5% w/w

Motor oil - used engine oil - 1 drop

Shoe polish - black Kiwi® brand - 1 stroke

Lipstick - red or bright pink - 1 stroke

[0046] Drops were applied using pipettes and strokes were applied using a 10mm spatula. All prepared swatches were left to set overnight prior to being tested.

[0047] Washing was conducted under European conditions using European washing machines at 40°C. A 'dummy' load was used, which consisted of 6 cotton terry nappies. 50g of non-biological Persil automatic washing powder was used. 9.5g of pre-spotter was applied to the stained swatch and left for one minute. This was then washed as normal in the washing machine together with the 'dummy' load. The washed swatches were then removed and ironed on the side opposing the stained surface. All testing was conducted in duplicate using non-biological washing powder, either with or without pre-spotter. An untreated swatch was also used to compare the 'before' and 'after' results.

[0048] The stain-removal performance was rated visually by a trained panel using a scale of 1 to 5, Where,

- 1 = little or no stain removal
- 5 = complete stain removal

[0049] The results were tabulated and converted into percentage stain removal in order to compare the overall performance.

Stains tested							
	Untreated	Α	В	С	D	E	Shout®
Vegetable oil Motor oil	1.0 1.0	4.0 2.0	4.5 3.0	4.5 3.0	4.5 4.5	4.5 4.5	3.5 3.0
Lipstick	1.0	1.5	3.0	3.0	3.0	2.5	1.5
Shoe polish TOTAL %Stain Removal	1.0 4.0 20	1.5 9.0 45	1.5 12.0 <i>60</i>	1.5 12.0 <i>60</i>	1.5 13.5 68	1.5 13.0 65	1.5 9.5 48

[0050] The optimum stain removal is given by the formulation with the lowest levels of the linear alcohol ethoxylate.

Claims

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- 1. A post-foaming cleaning composition comprising a post-foaming agent in an amount of about 20 to 40% by weight.
- 2. A composition according to claim 1 wherein the post-foaming agent is a volatile hydrocarbon.
- 3. A composition according to claim 1 or claim 2 wherein the composition is a microemulsion.
- 4. A post-foaming microemulsion cleaning composition comprising a hydrophilic component, a hydrophobic component, a surfactant component comprising at least 7% by weight aliphatic alcohol ethoxylate, and 20 to 40 % by weight of a volatile hydrocarbon post-foaming agent.
- 5. A packaged monophasic post-foaming cleaning composition comprising about 20 to 40% of a post-foaming agent.
- 6. A packaged composition according to claim 6 wherein the packaging is provided by an aerosol canister.
- 7. A packaged composition according to claim 5 or claim 6 wherein the post-foaming agent is a volatile hydrocarbon.
- 8. A packaged composition according to any of the claims 5 to 7 wherein the composition is a microemulsion.
- 9. A composition according to any of the preceding claims comprising 20 to 40 weight percent (wt%) deionised; 20 to 40 wt% n-butane; 15.75% to 19.25 wt% isoparaffinic hydrocarbon with a boiling point of 113 to 143°C; 7.5 to 9.3 wt% isopropanol; 6.0 to 13.0 wt% fatty alcohol ethoxylate (HLB 4 to 10); 2.5 to 3.1 wt % sodium di-alkyl sulphosuccinate (75%); 1.9 to 2.3 wt % of a fatty alcohol alkoxylate having a cloud point in water of between 28 and 42°C; 2.5 to 3.1% oleic acid; 0.32 to 0.38 wt% sodium hydroxide (47%); optionally 0.1 to 1.0 wt% of a fragrance material; and optionally 0.005 to 0.1 wt% of a preservative.
- 10. A composition according to claim 9 comprising 28.126 wt % Deionised water; 30 wt% n-butane; 17.5 wt% Isoparaffinic hydrocarbon Bpt.113-143; 8.4 wt% Isopropanol; 7.7 wt% C13-C15 linear alcohol ethoxylate 3EO; 2.8 wt% Sodium di-alkyl sulphosuccinate 75%; 2.8 wt% Oleic acid; 2.1 wt% Fatty alcohol alkoxylate having a cloud point in water of between 28 and 42°C; 0.35 wt% Sodium hydroxide 47%; 0.210 wt% fragrance; and 0.014 wt% preservative.
- 11. A method of pre-spotting a stained fabric comprising the step of applying thereto a composition as described in any of the preceding claims.

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EUROPEAN SEARCH REPORT

Application Number EP 01 11 5595

Category		ERED TO BE RELEVANT ndication, where appropriate,	Relevant	CLASSIFICATION OF THE	
Category	of relevant pass	to claim	APPLICATION (Int.Cl.7)		
X	US 4 954 286 A (SEF 4 September 1990 (1 * column 1, line 12 * column 2, line 19 * column 4, line 28 * claims 1,13 *	!-15 * !-32 *	1,2,4-7,	C11D3/18 C11D17/00	
X	EP 0 890 670 A (JOH 13 January 1999 (19 * claims 1-11; exam		1-3,5-8, 11		
X	US 4 362 638 A (SRA 7 December 1982 (19 * claims 1,2 *		1,2,5-7, 11		
X	GB 1 040 009 A (SHU 24 August 1966 (196 * page 1, line 55-7 *		1,2,5-7		
X	US 5 902 225 A (MON 11 May 1999 (1999-0 * claims 1,8 *		1,2,4-7	TECHNICAL FIELDS SEARCHED (Int.CI.7)	
D,X	US 5 962 396 A (GOM 5 October 1999 (199 * column 2, line 27 example I *	1,3-6,8			
x	WO 00 39273 A (UNIL HINDUSTAN LTD (IN); 6 July 2000 (2000-0 * claims 1,2,6,9,13	1,3,5,6, 8	,		
x	EP 0 586 295 A (NLN 9 March 1994 (1994- * page 4, line 53;	03-09)	1,5,6,11		
	The present search report has I		_		
MUNICH		Date of completion of the search 23 November 200	l Peni	entek, E	
X : partl Y : partl docu A : tech	ATEGORY OF CITED DOCUMENTS cularly relevant if taken alone cularly relevant if combined with another ment of the same category notogical background written discosure	T theory or princ E : earlier patent o after the filing o her D : cocument cite L : document cite	ple underlying the in locument, but publis fate d in the application i for other reasons	rvent on thed on, or	

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 01 11 5595

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

23-11-2001

Patent document dted in search report		Publication date		Patent family member(s)	Publication date	
US	4954286	A	04-09-1990	AU	619271 B2	23-01-1992
				AU	3268389 A	19-10-1989
				BR	8901723 A	21-11-1989
				CA	1322509 A1	28-09-1993
				JP	2014293 A	18-01-1990
				ZA	8902749 A	28-12-1990
ΕP	0890670	A	13-01-1999	EP	0890670 A2	13-01-1999
US	4362638	Α	07-12-1982	NONE	- 100 to 100	
GB	1040009	Α	24-08-1966	NONE		
US	5902225	Α	11-05-1999	AU	3896395 A	02-05-1996
				AU	5590296 A	10-10-1996
				WO	9611162 A1	18-04-1996
US	5962396	А	05-10-1999	AU	4206000 A	14-11-2000
				WO	0061710 A2	19-10-2000
				US	6004920 A	21-12-1999
				US	6051542 A	18-04-2000
WO	0039273	Α	06-07-2000	AU	1874400 A	31-07-2000
				EP	1141223 A1	10-10-2001
				MO	0039273 A1	06-07-2000
EP	0586295	Α	09-03-1994	FR	2695133 A1	04-03-1994
				EP	0586295 Al	09-03-1994

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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